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Patrick Ruth (ERC); Brent Viers (PRSM); Rusty Blanski (PRSM); Andre Lee, "Effects on Processing by Drop-In Modifiers in Nano-Composite Polymers"

SAMPE Spring Meeting (General Audience)
(Long Beach, CA, 12-15 May 2002) (Deadline: ASAP) **(Statement A)**

EFFECTS ON PROCESSING BY DROP-IN MODIFIERS IN NANO-COMPOSITE POLYMERS

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ABSTRACT

One of the greatest barriers in transitioning new or altered polymers to commercial application is the cost of new equipment for processing or the cost of developing parameters for the new material. One solution is developing "drop-in" modifiers that alter the properties of presently used materials without altering the processing parameters or requiring exotic equipment. Over the last decade the Air Force Research Laboratory has studied how the Polyhedral Oligomeric Silsesquioxanes (POSS) can be incorporated as blendables in industrial polymers like polypropylene to improve properties without sacrificing the ease of processing. This talk will detail the processing method (drying, blending, extruding and molding) of Octamethyl POSS/ polypropylene nanocomposites. The degree of compatibility was established with visual methods.

KEY WORDS: Nanocomposites, POSS, Isotactic Polypropylene

1. INTRODUCTION

The goal of this paper is to show examples of adding modifiers to polymers to enhance properties without altering processing parameters or processing equipment.

Consider that different types of plastic materials individually have properties that specifically address certain needs. For example, polypropylene has excellent chemical resistance and is very inexpensive. A problem arises when one material is required to address needs normally handled by several separate materials. Polypropylene may be chemically resistant, but has a relatively low use temperature.

There are two paths that can be followed in order to solve this sort of problem. One path is to develop completely new materials that fit the need, like polyamides. The other path is to alter or modify the material being used. The difficulty of following the first path is the cost in time, materials and human capital to synthesize a new plastic. The second cost inhibiting factor of a new material is the cost to transition it into industry. In the

laboratory, the new material may have the wanted properties, but it may also have very unattractive features like sensitivity to stress fractures from processing or an extremely high and narrow processing window. In this case the new material is no better than those already available.

Consideration of the "new material" path makes the "modification" path seem more feasible. The modification path involves altering the polymer either chemically or intimately blending it with another material that will produce or accentuate the desired properties. The key is to bring out the best properties of both materials while reducing the undesired properties. The focus of this paper is mechanical blending. The normal blending combinations of materials are polymer/polymer, polymer/filler or polymer/modifier. The pitfall of blending is compatibilization. It is rare to find two different materials that intimately mix with one another. Fillers are materials in which miscibility is not a crucial feature. Fillers usually behave as viscosity modifiers or act as composites to improve mechanical properties. Polymer/polymer blends on the other hand depend on compatiblization to achieve a fine dispersion. Almost from the beginning of polymer history graft and block polymers were used as interfacial agents in polymer blends. The compatibilizer contains sections that have the same structure as the two polymers to be blended. The compatibilizer controls the size and the adherence of the polymer regions.

A modifier can be defined as a material in which one part is a nano-filler and the other part is a chemically attached functional group that acts as a compatibilizer (It is usually similar to the polymer). In the past decade, the Air Force Research Laboratory has been investigating effects of blending Polyhedral Oligomeric Silsesquioxanes (POSS) to single polymer matrices. POSS is a silicone-oxygen nano-structure with the opportunity to attach functional groups. The blend that will be used as an example is polypropylene with Octa-methyl POSS (Me_8T_8) in 10 weight percent.

In discussing the properties of this blend there is a caveat. There are three major variables that can determine the quality of the properties of a plastic. The first is the material preparation before processing (contaminants and moisture). The second is the processing parameters (Temperature, Time and Pressure). The third is the machine. The type of mixer can greatly influence the physical properties of plastics. The mixer used for this demonstration the DACA Twin-Screw Extruder. The focus of this paper is to follow the path to incorporate Me_8T_8 in to polypropylene.

"into" one word

2. MATERIALS

The two materials used in this experiment are isotactic polypropylene and Octa-methyl POSS. Specifically the polypropylene is Dow Inspire Polypropylene H704-04 (GMID:00125871, lot# 0B2801MB05). As mentioned before, the pleasing characteristics of polypropylene are its chemical resistance, its ease of processing and its very low cost.

The second material is a POSS monomer with eight methyl groups attached. Its name is Octa-Methyl T_8 and will be expressed in the short hand Me_8T_8. It has a molecular weight of 536.96 mol/gm and can be obtained from Hybrid Plastics.

3. EXPERIMENTAL

3.1 Sample Preparation Polypropylene is one ~~on~~ of the least hygroscopic plastics in commercial use. But it is good practice to thoroughly dry all polymers before processing. The drying process practiced for this experiment is to place about 200 grams of the polymer in a clean glass dish inside a heated vacuum oven. The temperature selected is roughly 15°C below the onset of the melt of the polymer. In this case the oven was set to 120°C. The polymer is in the oven at this temperature for approximately one hour. The Me_8T_8 was dried under the same conditions.

3.2 Brabender Mixing: A Brabender Plasticorder mixer has been used to form large batches (30 g) of the PP/Me_8T_8 POSS blends. The mixing time was set to be 3 minutes at 100 R.P.M. and at 177°C. The Brabender is thought to have a very low shear mixing, and would be expected to have the poorer dispersion than similar DACA twin screw extruder processing. Brabender mixed POSS/PP blends appear to be less homogeneous than similar DACA blends. The processing properties of Brabender mixing will be the subject of further research.

ee Figure 1)

3.3 DACA Twin-Screw Extruder This machine holds between 3 and 5 grams of material. The screws are co-rotating, 10.5 cm long and conical (1cm diameter at the feed section and 0.4 cm diameter at the end). This machine has read-out for R.P.M., load (N), and Torque (Nm). An interesting feature of this machine is a channel cut in the barrel that leads from the exit end of the screw back to the feed section. This allows longer mix times to mimic a larger machine. A valve directs the flow between the exit and the channel. A better description can be found at WWW.DACA.com.

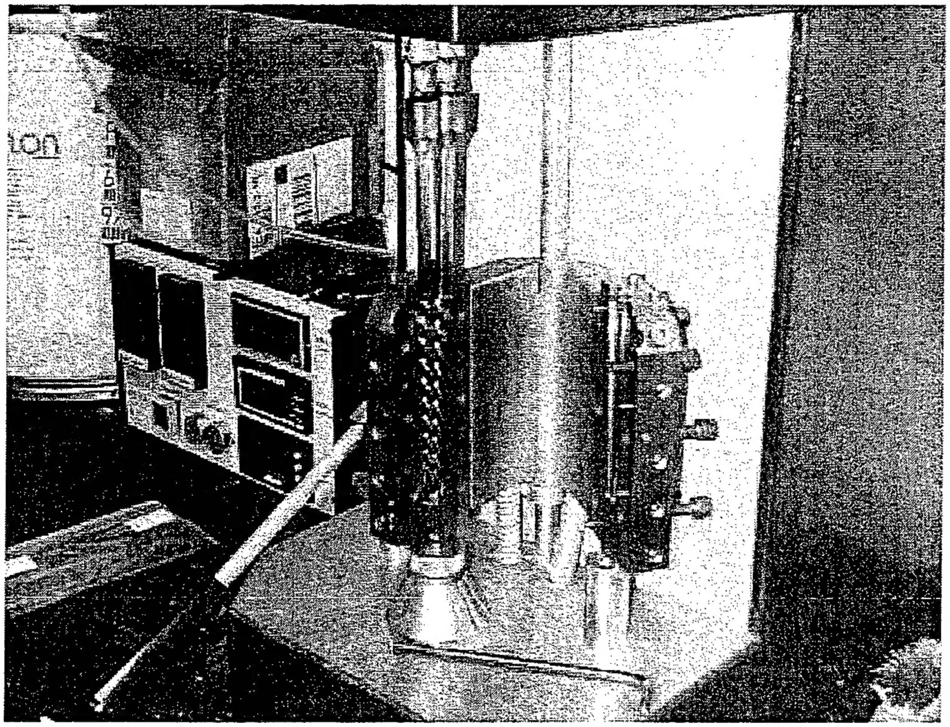

Figure 1 A lab scale DACA twin screw extruder

3.3.1.1 DACA Processing Parameters The temperature of the DACA was set to 177° C. The screw speed was set to 100 R.P.M. The mix time was 3 minutes. This mix time was chosen because DMTA tensile tests showed samples subjected to longer and shorter mix durations did not perform as well as those processed for a 3 minute duration. The polypropylene/Me_8T_8 10% wt. was mixed in 4 gram batches.

3.3 Methods for Evaluation The samples were examined in two ways to assume intimate blending. First the extrudate was inspected for clarity, turbidity, bubbles and chunks. These observations were compared to the pure polypropylene standard. During mixing the Load and Torque were noted to compare the difficulty of forcing the two phases together. Then a small piece of the extrudate was pressed into a thin film. The films were hot pressed under these conditions: (step 1) 205°C for 10 minutes at 0.04316 MPa, (step 2) cool to 27°C at 6.8947 MPa and hold for 10 minutes. The films were approximately 0.15 mm thick.

4. RESULTS AND DISCUSSION

4.1 Load and Torque During Mixing Table 1 is a chart showing the Load and Torque as it was observed from the read out displays on the DACA twin-screw extruder. The chart compares materials that were dried before processing to materials in which the drying procedure was skipped. It also shows the difference in difficulty the machine must work in order to blend these materials. Mix 1 and 2 are pure polypropylene. The difference is the polypropylene in mix 2 was dried using the method mentioned above.

Mix 2 is of polypropylene that had been exposed to the 14% humidity of the laboratory for several days. Mixes 3 through 6 are combinations of dried or not dried Me_8T_8 and dried or not dried polypropylene. The Torque reading is a direct measurement of the electrical current of the motor. The load is directly related to the amount of pressure that must build up to force the material through the small screw flights at the exit end of the extruder. Both are related to the degree of dispersion. As the material melts and the polymer/monomer regions are becoming smaller and more dispersed the load and the torque go down in value until they reach a steady state. This steady state number represents the maximum amount of dispersion this material will achieve by this method.

Mix #	Material Percentage				Load (N)				Torque (Nm)			
	PP		Me_8T_8		Mix Duration (min)				Mix Duration (Min)			
	Dried	Not Dried	Dried	Not Dried	0	1	2	3	0	1	2	3
1		100			3500	3200	3100	3000	4.65	4.50	4.30	4.10
2	100				3500	3100	3000	2900	4.60	4.45	4.25	4.05
3	90		10		3200	3000	3000	2850	4.80	4.40	4.25	4.20
4	90			10	3200	3100	3100	2900	4.60	4.45	4.20	4.25
5		90	10		3500	3250	3200	3000	5.00	4.55	4.45	4.30
6		90		10	3400	3200	3100	3000	4.60	4.45	4.34	4.00

Table 1 Twin Screw Processing Parameters for Me8T8/iPP nanocomposite blends.

4.2 Visual Inspection The DACA load and torque parameters suggest that addition of POSS doesn't affect the processing of the materials. However, it is important to have a visual comparison of the blends and pressed films are used as a measure of the compatibiltiy

4.2.1 Observation of the Extrudate "Dried" polypropylene is clear at the exit port of the extruder. As it cools it becomes translucent. "Not dried" polypropylene has the same translucent appearance as solid dry propylene in both the melt and solid state. All of the other blends are opaque white after they have cooled. All except Mix 3 (dried

polypropylene and dried Me_8T_8) are just as opaque in the melt as they are after cooling. Mix 3 was slightly cloudy at the exit nozzle of the extruder then turned opaque.

4.2.2 Observation of a Thin Film Each of the blends were hot pressed into thin films 0.15 mm thick. The films are clear to the touch. Below is a scanned image of a film with each of the blends pressed in strips. The scan color was inverted to make identification of the POSS particles easier. The black specks are regions of Me_8T_8. Films 1,2 and 3 appear very homogenous. Films 4, 5 and 6 each have at least one component that was not dried prior to processing. 5 and 6 have obvious large incompatible regions of POSS. This is the first step of producing a drop-in modifier. Once the conditions for producing compatible material are established, the next step is to test the mechanical properties and to correlate these properties to the observed filler distribution.

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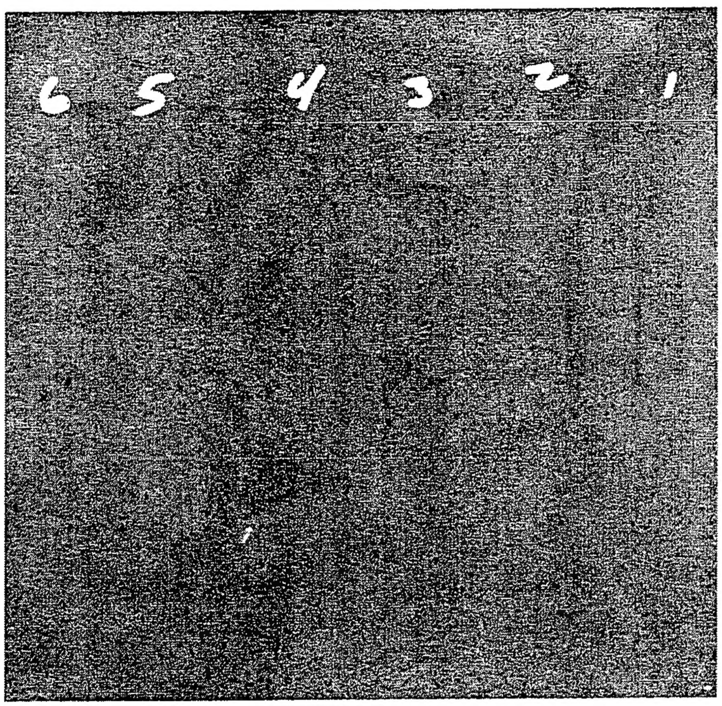

Figure 2 Pressed film of DACA extruded POSS/PP blend variants (see Table 1 for details)

5. CONCLUSIONS

Me_8T_8 does seem to be very melt compatible with isotactic polypropylene under special circumstances of dried materials and twin screw mixing/extrusion. The extra load/torque to mix the polymer with the POSS is increased if either of the components is not dried. Visually, the most compatible of the mixes is number 3 where both POSS and PP components were dried. The extruded rod nearly as clear as pure polypropylene in the melt. Melt pressed thin films of number 3 can be clear and have no POSS particles, although films determined to be incompatible will have large POSS particles.

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